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Method Development and Evaluation of Draft Protocol for Measurement of Condensible Particulate Emissions. Test Report

Entropy Environmentalists, Inc., Research Triangle Park, NC

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The report describes the development and evaluation of a draft protocol for measuring condensible particulate matter (CPM) emissions. An impinger catch approach was evaluated in the laboratory and at wood-fired and coal-fired boilers. The report summarizes the approach and major findings and recommendations which resulted from the study. Test results and statistical analysis of the results are presented.

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METHOD DEVELOPMENT AND EVALUATION OF DRAFT PROTOCOL FOR MEASUREMENT OF CONDENSIBLE PARTICULATE EMISSIONS

CONTROL TECHNOLOGY CENTER

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Emission Standards Division
Office of Air Quality Planning and Standards
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PREFACE

The CTC was established by EPA's Office of Research and Development (ORD) and Office of Air Quality Planning and Standards (OAQPS) to provide technical assistance to State and Local air pollution control agencies. Three levels of assistance can be accessed through the CTC. First, a CTC HOTLINE has been established to provide telephone assistance on matters relating to air pollution control technology. Second, more in-depth engineering assistance can be provided when appropriate. Third, the CTC can provide technical guidance through publication of technical guidance documents, development of personal computer software, and presentation of workshops on control technology matters.

The technical guidance projects, such as this one, focus on topics of national or regional interest that are identified through contact with State and local agencies. In this case, the CTC became interested in evaluating a test method for measuring condensible particulate matter (CPM) in response to a number of requests from State and local air pollution control agencies. This document presents laboratory and field evaluations on the impinger catch method. The impinger catch is the back half portion of the EPA Method 5 sampling train. The principal objective of this evaluation was to determine the adequacy of the test method and produce documentation to support it. This was accomplished through laboratory experiments and field tests.

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is planning to propose in Appendix M, 40 CFR Part 51, the impinger catch method for measuring condensible particulate matter (CPM). To support this action, the Emission Measurement Branch (EMB), Office of Air Quality Planning and Standards, EPA, contracted with Entropy Environmentalists, Inc., to evaluate the impinger catch approach for measuring CPM. This report details the laboratory and field evaluations done under EPA Contract Nos. 68-02-4336 (Work Assignments 23 and 34) and 68-D-90055 (Work Assignment 13).

1.1 BACKGROUND

EPA considers all CPM to be PM_{10}, i.e., particulate matter (PM) of 10 μm or less in aerodynamic diameter. Since the current PM_{10} test methods measure only in-stack PM, EPA concluded that a CPM method was vital.

A candidate method was formulated based on a literature review[1-9] and consideration of the ease of execution, availability of equipment, analytical detection limits, sensitivity and range, and sample preparation. EPA concluded that the impinger catch approach would be most desirable because it (1) allows the determination of both filterable PM and CPM simultaneously, (2) uses existing methodology and equipment, and (3) was being used by several State agencies.

The impinger catch is the back half portion of the EPA Method 5 train. The determination of CPM involves: (1) purging the impinger solution with an inert gas after the test run; (2) extracting the impinger solution to separate the organic from the inorganic CPM fraction; (3) drying the organic fraction at room temperature and the inorganic fraction at 105°C; and (4) weighing the residues.

Before this method could be proposed, EPA felt that several areas needed to be investigated. They were as follows:

(1) Formation of "false" CPM. Since gases are bubbled through water, noncondensible gases may react with other gases or condensibles to form CPM that would not have otherwise formed. The most notable case of this is the oxidation of SO_2 to form $SO_4^=$. The SO_2 dissolves in water to form H_2SO_3, which may oxidize to form H_2SO_4. This $SO_4^=$ would then be counted as CPM. One document[1] showed that purging the impinger solution with air immediately after sampling effectively removed SO_2. However the air purge raised questions concerning the possible conversion of SO_2 to sulfur trioxide (SO_3); therefore, further evaluation of the effectiveness of an air or N_2 purge to remove SO_2 was needed.

(2) Extraction solvents. Three solvents are commonly specified by State agencies for extracting CPM from impinger solutions: methylene chloride ($MeCl_2$), chloroform-ether (C-E), and Freon. The effectiveness of these solvents needed to be evaluated.

(3) Weighing to a constant weight. The hygroscopic nature of H_2SO_4 makes weighing of the residue to a constant weight difficult. In one State procedure, NH_4OH is added to the impinger solution to form the $SO_4^=$. The accuracy of this approach needed to be documented.

1.2 OBJECTIVES

The principal objectives of the evaluation were to determine the adequacy and produce documentation to support the test method, revise the candidate method based upon the results of the laboratory experiments, and validate the method in field tests and revise the method, if necessary.

1.3 BASIC TECHNICAL APPROACH

The basic approach consisted of two phases. The first was to evaluate the candidate method in the laboratory as follows: (1) Determine the effectiveness of the three different solvents being used by some State agencies to extract the organic fraction at three different pH levels; (2) determine the effectiveness of the N_2 purge to remove dissolved SO_2 from the impinger solution; and (3) revise the candidate method based on the laboratory evaluation.

The second phase was to evaluate the revised test method in the field as follows: (1) Determine the precision of the revised method at three different field sites; (2) conduct any other experiments in the laboratory or in the field to resolve the resulting questions; and (3) finalize the revised test method into Federal Register format.

2.0 CONCLUSIONS AND RECOMMENDATIONS

As a result of the laboratory and field evaluations of the impinger catch approach for determining CPM, the conclusions and recommendations are as follows:

1. When SO_2 is present at significant levels, the sample should be purged with N_2 at a rate of 20 liters/min for 60 minutes immediately after the end of the test run. An air purge is not recommended, but could be allowed.

2. If SO_2 is not present at significant levels, a purge is not necessary.

3. If the pH of the sample is less than 4.5, then NH_4OH should be added to the sample to stabilize H_2SO_4 and provide accurate weighing.

4. When NH_4OH is added, the amount retained by the sample should be determined from the sulfate ($SO_4^=$) analysis using ion chromatography (IC). The mass of NH_4OH retained may also be determined by titrating the sample to a pH of 7.0 using 0.1 N NH_4OH and a pH meter.

5. If NH_4OH is to be used, the sample should be dried at 105°C and the residue resuspended before adding the NH_4OH. The sample may also be analyzed for chlorides (Cl^-) following the final weight determination and the amount of ammonium chloride (NH_4Cl) may be subtracted from the final weight.

6. $MeCl_2$ is recommended as the organic extraction solvent. C-E is acceptable as a secondary choice. Freon is unacceptable.

7. When both organic and inorganic CPM is being determined, the pH of the sample need not be adjusted before extraction. The extraction should be repeated three times.

8. Four Method 5 type impingers should be used in the sampling train as follows: Two should be tipped (Greenburg-Smith design) and the last two should have the modified tip. In each of the first three impingers, 100 ml of deionized distilled water should be added, and 200 g of silica gel should be placed in the fourth.

9. The precisions (standard deviations) for the draft method based on tests at a wood waste boiler and two coal-fired boilers are 13.0 ± 2.1 mg/m^3, 3.5 ± 1.1 mg/m^3, and 39.5 ± 9.0 mg/m^3, respectively. Further studies are recommended to determine whether precision of weighing low loadings (less than 10 mg) can be improved.

10. The method may not be applicable at sources that contain high levels of ammonia (e.g., when ammonia injection is used as a control technique). For such sources, the amount of NH_4Cl may be subtracted from the final weight. Additional studies at sources with ammonia emissions are recommended to determine if the N_2 purge is still effective in removing the SO_2 from the impinger solution under these conditions.

3.0 LABORATORY EVALUATION

This section describes the experimental design of the laboratory evaluation, data, and conclusions.

To provide typical sample matrix effects, samples of impinger contents from previously conducted Method 5 test runs (mostly from studies conducted for EPA) were used. These samples had not been subjected to the N_2 purge.

The sources of the samples were a coal-fired boiler, an oil-fired boiler, a mass burn municipal waste combustor, a refuse-derived fuel municipal waste combustor, and wood-waste boilers.

3.1 EVALUATION OF ORGANIC MATTER ANALYSIS

In the laboratory, two parameters of the organic CPM analysis were evaluated: (1) the effectiveness of organic extraction by $MeCl_2$, C-E, and Freon, and (2) the effect of pH on extraction. The effect of pH was evaluated because of the different solubilities of organics. An alternative technique, solid phase extraction (SPE), was also evaluated because of its potential to (1) reduce the time of extraction step, (2) reduce the amount of solvent to be evaporated 50-fold, and (3) increase the analytical precision.

To provide sufficient volume of impinger contents for comparisons of the solvent extractions, the impinger contents from all sample runs within a test series were combined into a single sample. The source categories used were a wood-fired boiler (high in organic matter and low in inorganic), and a coal-fired boiler (low in organic matter and high in inorganic).

The steps used to compare the different solvents at different pH levels are given below.

For the coal-fired boiler, the samples were treated as follows:

1. The sample was filtered through a 0.2 μm Teflon filter and then the pH was determined.

2. The sample was shaken vigorously and divided into 8 equal aliquots.

3. Aliquots 1, 2, and 3 were treated as follows:

   a. Each aliquot was extracted using separatory funnels at the pH of the sample (2.0) with $MeCl_2$, C-E, or Freon. Each aliquot was extracted four times.

   b. A 5-ml portion of the aqueous fraction was analyzed for Cl^-, nitrates (NO_3^-), and $SO_4^=$ by IC.

   c. NH_4OH was added to the remaining aqueous fraction. This fraction was dried, desiccated for 24 hours, weighed, and then reweighed after two additional hours. To assure that the

residue was completely dry, they were reheated, cooled, desiccated overnight, and reweighed.

d. The residue from Step 3c was then redissolved in water and analyzed for Cl^-, NO_3^-, and $SO_4^=$.

4. Aliquots 4 and 5 were treated as follows:

a. Each aliquot was extracted as in Step 3a above with $MeCl_2$ or Freon, and analyzed for anions as in Step 3b.

b. The aqueous fraction was then adjusted to a pH of 12 with NH_4OH solution, reextracted as described in Step 3a above, and then treated as in Step 3c without further addition of NH_4OH.

5. Aliquot 6 was treated as follows:

a. One sample aliquot was passed through a bonded octadecyl silic (C-18) sorbent.

b. The organic matter on the C-18 sorbent was eluted sequentially with four separate 2-ml portions of methanol. Each portion was analyzed separately.

c. The aqueous fraction (part passing through the C-18 sorbent) was analyzed as in Step 3b - 3d above.

6. Aliquots 7 and 8 were treated as follows:

a. The sample aliquots were adjusted to a pH of 7 with NaOH.

b. The samples were then treated as in Step 5b above.

The results from the coal-fired boiler test are presented in Table 3.1. As expected, the fraction of organic CPM in the samples was low. Because of the small amount of mass in each organic sample fraction, the relative precision was poor. In the cases where 0.0 mg is shown for sample weight, the actual weight may have been negative. However, the organic CPM weights of 1 to 2 mg constituted only about 1 percent of the inorganic CPM weights of 170 to 183 mg and thus will not affect the precision of the total CPM determinations. The precision of the analysis for total CPM from the coal-fired boiler was 178 ± 5 mg. The standard deviation was 2.8 percent.

The variable results for samples extracted at a pH of 2 could not be traced to any particular solvent. When the sample was adjusted to a pH of 12, some additional organics were extracted but the amount was not significant.

The most significant discovery was that the level of the Cl^- (40 to 57 mg, which was about equal to the mass of $SO_4^=$) in the aqueous fraction both before and after it was taken to dryness was unexpectedly high. No NO_3^- were found in the samples.

TABLE 3.1. ORGANIC RESULTS FOR SAMPLE L FROM A COAL-FIRED BOILER

Aliquot No.	1 4	2 5	3	6	7 8
				C-18	
Fraction	Trichloro-trifluoro-ethane	Methylene Chloride	Chloroform/ Diethylether	pH 2	pH 7
	Extraction at sample pH (2.0)[a]				
First extract	0.0 0.5	0.2 0.3	0.4	0.4	0.6 0.6
Second extract	0.2 0.5	0.5 0.4	0.2	0.5	0.6 0.7
Third extract	0.4 0.4	0.2 0.4	0.7	0.2	0.6 0.4
Fourth extract	0.4 0.5	0.5 0.7	0.6	0.2	0.2 0.0
Total	1.0 1.9	1.4 1.8	1.9	1.3	2.0 1.7
	Extraction at pH of 12				
First extract	0.0	0.6			
Second extract	0.0	0.0			
Third extract	0.1	0.0			
Fourth extract	0.0	0.0			
Total	0.1	0.6			
Total Organic	1.0 2.0	1.4 2.4	1.9	1.3	2.0 1.7
	Gravimetric Results for Aqueous Fraction				
Aqueous Residue	192 195	196 198	193	193	
$(NH_4)_2SO_4$ Corr.	175 180	178 183	173	170	
Total Condensibles	176 182	179 185	175	172	
	Aqueous Fraction Ion Chromatography Results				
Chloride	52.5 40.7	54.0 40.2	54.0	57.0	
Sulfate	50.3 43.0	51.7 41.9	58.4	64.6	
	Ion Chromatography Results of Resuspended Residue				
Chloride	46.5	47.9		47.9	
Sulfate	49.5	51.5		52.2	

[a]Except for C-18 extractions, which were extracted at the pH shown above.

Note: All results are in mg and represent the total for a 150 ml sample aliquot.

The combined mass of the $SO_4^=$ (42 to 65 mg) and Cl^- (40 to 57 mg) totalled only about one-half of the inorganic CPM (170 to 183 mg). $SO_4^=$ were anticipated to constitute the majority of the inorganic CPM. Since this was not the case, determining only the amount of SO_3 in the emissions to represent CPM is not a viable approach.

For the wood-fired boiler, the samples were treated as follows:

1. The sample was filtered through a 0.2 μm Teflon filter and then the pH was determined.

2. The sample was shaken vigorously and divided into 6 equal aliquots.

3. Aliquots 1, 2, and 3 were treated as follows:

   a. Each aliquot was extracted using separatory funnels at the pH of the sample (4.0) with $MeCl_2$, C-E, or Freon. Each aliquot was extracted four times.

   b. NH_4OH was added to the aqueous fraction. This fraction was dried, desiccated for 24 hours, weighed, and then reweighed after two additional hours. To assure that the residue was completely dry, they were reheated, cooled, desiccated overnight, and reweighed.

   c. Before adding the NH_4OH, a 5-ml portion of the aqueous fraction of one of the aliquots was taken and analyzed for Cl^-, NO_3^-, and $SO_4^=$ by IC. After this aliquot was dried and weighed, the residue was redissolved in water and analyzed for the same anions.

4. Aliquots 4 and 5 were treated as follows:

   a. Each aliquot was adjusted to a pH of 2 with concentrated nitric acid and were extracted as above with Freon or C-E.

   b. The aqueous fraction was then adjusted to a pH of 12 with NaOH. One aliquot was reextracted as described above and the other was extracted only once.

5. Aliquot 6 was treated as follows:

   a. The sample aliquot was passed through a bonded octadecyl silic (C-18) sorbent.

   b. The organic matter on the C-18 sorbent was eluted sequentially with four separate 2-ml portions of methanol. Each portion was analyzed separately.

   c. The aqueous fraction (part passing through the C-18 sorbent) was analyzed as in Step 3b above. After this fraction was

taken to dryness and weighed, the residue was redissolved in water and analyzed for Cl^-, NO_3^-, and $SO_4^=$ by IC.

Table 3.2 presents the results from the wood-fired boiler test. The mass of organic CPM was high as had been anticipated. However, the mass of inorganic CPM in the aqueous fraction was significantly higher than had been expected. The amount of $SO_4^=$ and Cl^- was low, and NO_3^- were not found.

The pH levels of 2 and 4 did not affect the solvent extractions. $MeCl_2$ yielded 16 mg (pH of 4), C-E yielded 15.5 (pH of 4) and 16.5 mg (pH of 2), and C-18 yielded 15.6 mg (pH of 4). Freon gave 1.9 (pH of 4) and 2.6 mg (pH of 2). Extractions at a pH of 12 gave an additional 25 percent CPM for all solvents.

Although Freon extracted only about 2 of the 16 mg of organics, the majority of the organics left in the aqueous fraction were analyzed as inorganics. The total CPM for the samples extracted with Freon was the same for those samples extracted with the other solvents. Therefore, Freon was considered to be an unacceptable solvent if only organic CPM is desired but could be acceptable if total CPM was being measured. However, since Freon is a chloroflorohydrocarbon, its use is not recommended.

The precision of the total CPM analysis for wood-fired boiler was 46.6 ± 2.0 mg, which translates to a relative standard deviation of 4.3 percent.

Based on the results of both the coal-fired and wood-fired boilers, three extractions are considered to be sufficient, the pH of the sample need not be adjusted if total CPM (i.e., organic plus inorganic CPM) is being determined, but if only the organic CPM is being determined, the samples should be extracted at both pH's of 2 and 12.

3.2 EVALUATION OF INORGANIC CPM SAMPLING AND ANALYSIS

This part of the CPM method evaluation focused on the following: (1) Is organic material removed during the purging process? (2) Can the SO_2 converted to sulfites in the impingers be removed by purging? (3) Is SO_2 converted to $SO_4^=$ during sampling? (4) What portion of the inorganic matter is $SO_4^=$? (5) Can inorganic CPM be gravimetrically determined accurately when H_2SO_4 is a significant portion of the aqueous fraction?

The overall scheme of the laboratory experiment is shown in Figure 3.1 and is described below. Samples from combustion sources with high levels of SO_2 were used for this experiment.

1. The laboratory setup (see Figure 3.2) included an SO_2 gas cylinder and a N_2 gas cylinder, two impingers for the sample evaluation, one impinger to remove SO_2, one impinger to remove moisture, an SO_2 analyzer, and a hydrocarbon analyzer. Excess SO_2 was vented outside. The evaluation was conducted on nine samples and a water blank (see Table 3.3).

TABLE 3.2. ORGANIC RESULTS FOR SAMPLE A FROM A WOOD-FIRED BOILER

Aliquot No.	1	4	2	3	5	6
Fraction	Trichloro-trifluoro-ethane		Methylene Chloride	Chloroform/ Diethylether		C-18
	pH 4	pH 2	pH 4	pH 4	pH 2	pH 4
Extraction at Sample pH 4 and Adjusted pH 2						
First extract	1.4	1.7	10.8	11.8	12.2	14.0
Second extract	0.4	0.0	2.3	1.4	2.4	1.5
Third extract	0.1	0.7	1.6	1.4	0.8	0.0
Fourth extract	0.0	0.2	1.3	0.9	1.1	0.1
Total	1.9	2.6	16.0	15.5	16.5	15.6
Extraction at pH of 12						
First extract		0.8			1.4	
Second extract					1.4	
Third extract					0.0	
Fourth extract					1.2	
Total		0.8			4.0	
Total Organic	1.9	3.4	16.0	15.5	20.5	15.6
Gravimetric Results for Aqueous Fraction						
Aqueous Residue	46.4		33.9	32.3		36.6
$(NH_4)_2SO_4$ Corr.	43.4		30.9	29.3		33.6
Aqueous Fraction Ion Chromatography Results						
Chloride	NA[a]		NA	0.9		NA
Sulfate	NA		NA	0.6		NA
Ion Chromatography Results of Resuspended Residue						
Chloride	NA		NA	1.3		1.1
Sulfate	NA		NA	5.7		5.5
Total Condensibles	45.3		46.9	44.8		49.2

Note: All results are in mg and represent the total for a 150 ml sample aliquot.

[a]Not analyzed.

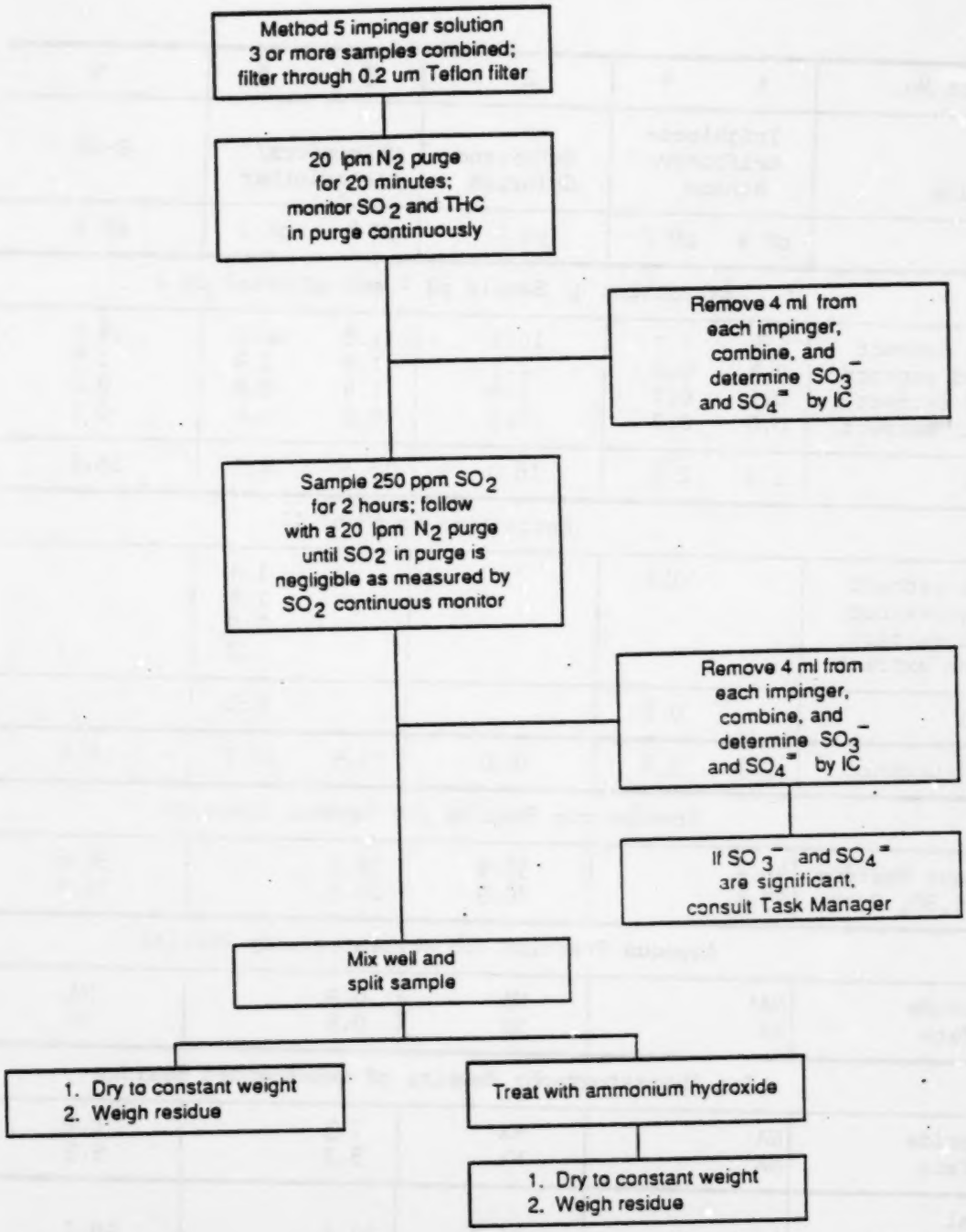

Figure 3.1. Scheme for evaluation of inorganic matter sampling and analytical procedures.

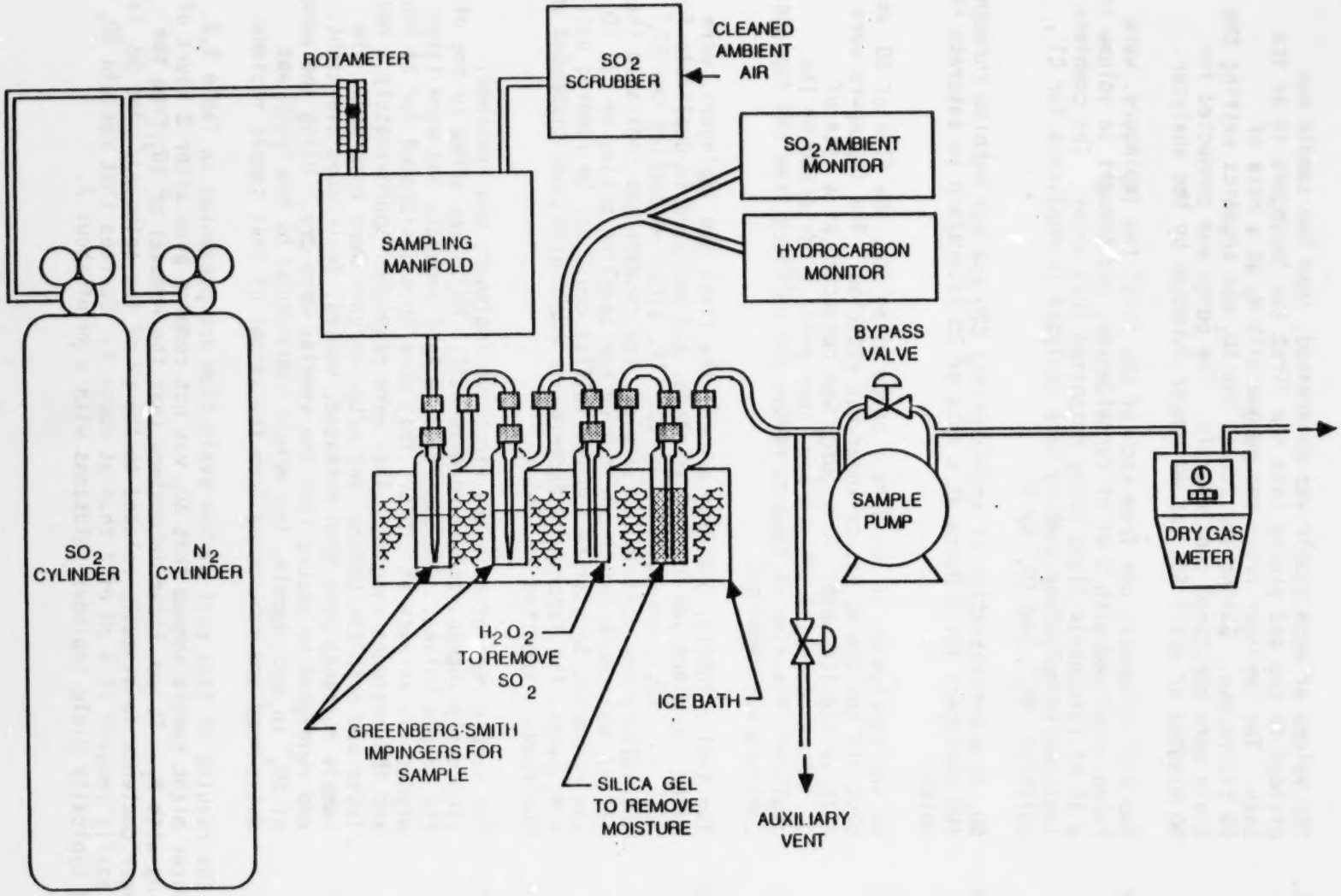

Figure 3.2. Laboratory setup for N_2 purge and SO_2 sampling.

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2. The volume of each sample was determined, then the sample was divided in two and placed into the first two impingers in an ice bath. The impinger train was purged with N_2 at a rate of 20 liters/min. During the purge, the SO_2 and organics exiting the train were monitored continuously. The purge was conducted for 60 minutes or until SO_2 was no longer detected by the analyzer.

3. Two 4-ml aliquots, one from each of the first two impingers, were taken, combined with 1 ml of formaldehyde, and brought to volume in a 10-ml volumetric flask using deionized (DI) water. The combined impinger/formaldehyde samples were analyzed in duplicate for Cl^-, sulfites, NO_3^-, and $SO_4^=$ by IC.

4. SO_2 at a concentration of approximately 250 ppm was bubbled through the impingers for 2 hours at a rate of 20 liters/min to saturate the water.

5. At the conclusion of the 2-hour purge using SO_2, the flow of SO_2 was shut off and the N_2 gas cylinder was attached. The impingers were left in the ice bath. A N_2 purge was conducted at a rate of 20 liters/min until SO_2 was low (near zero) as detected by the analyzer. The time it took to remove the sulfites from the impinger contents was recorded.

6. Two 4-ml aliquots, one from each of the first two impingers, were taken, combined and diluted as above, and analyzed in duplicate for $SO_4^=$, Cl^-, NO_3^-, and sulfites by IC. If, after conducting the $SO_4^=$ and sulfite analyses on two samples, the results had indicated that (1) SO_2 was converted to $SO_4^=$ during the sampling phase, or (2) SO_2 was converted to sulfite and the sulfite could not be removed using a N_2 purge, the laboratory experiments would have been suspended and the results reported to EPA.

7. The sample remaining in the first two impingers was combined, vigorously shaken, and divided in half. NH_4OH was added to one of the sample halves. The samples were kept separate and were taken to dryness in an oven at 110°C. They were then desiccated for 24 hours and the residues weighed. They were reweighed approximately 2 hours later and both the before- and after-weights were recorded. The sample residues were then reheated, cooled, desiccated overnight, and reweighed to assure that the samples were dry. Using the amount of $SO_4^=$ in each sample, the weight contributed by the NH_4OH was determined and subtracted from the weight of that sample residue.

The results of this part of the evaluation are presented in Table 3.3. The water blank sample showed that SO_2 was not removed even after 2 hours of purging with N_2. It was later determined that the removal of SO_2 from the impinger contents is directly related to the pH of the solution. The SO_2 is more easily removed at a pH of 2 than at above 4. Sources that contain SO_2 would typically yield impinger solutions with a pH of about 2.

TABLE 3.3. RESULTS FROM EVALUATION OF INORGANIC CONDENSIBLE DETERMINATION

	Residue Weights (mg)			IC Results (mg)[a]		Impinger Concentrations (mg/ml)			
	Untreated	NH_4OH Treated	NH_4OH[b] Corrected	as NH_3 salt	$SO_4^=$	$SO_4^=$	$SO_3^=$	Cl	NO_3^-
Run A: Blank - Required 120-minute N_2 purge to reach 0.24 ppm SO_2									
Before						ND	ND	ND	ND
After	5.8	6.4	5.7	3.0	2.4	0.0099	0.0059	ND	ND
Difference					2.4				
Run B: Coal-fired boiler - Required 30-minute N_2 purge to reach 0.08 ppm SO_2									
Before					15.8	0.0613	ND[c]	0.162	0.0026
After	42.4	52.8	46.6	24.6	18.2	0.0752	ND[c]	0.173	0.0023
Difference					2.4	0.0139		0.011	
Run C: Coal-fired boiler - Required 40-minute N_2 purge to reach 0.08 ppm SO_2									
Before					17.6	0.0615	ND[c]	0.1524	0.0019
After	48.2	53.0	46.5	25.7	18.5	0.0684	ND[c]	0.1642	0.0026
Difference					0.9	0.0079		0.0118	
Run E: Coal/oil-fired boiler - Required 60-minute N_2 purge to reach 0.1 ppm SO_2									
Before					20.1	0.0754	ND[c]	0.0402	ND
After	20.6	37.6	30.9	26.5	19.4	0.0774	ND[c]	0.0402	ND
Difference					-0.7	0.002		0.0	
Run F: Coal/oil-fired boiler - Required 40-minute N_2 purge to reach 0.08 ppm SO_2									
Before					16.8	0.0665	ND[c]	0.1237	ND
After	29.8	48.4	42.0	25.4	17.9	0.0760	ND[c]	0.1287	ND
Difference					1.1	0.002		0.005	
Run H: RDF incinerator - Required 40-minute N_2 purge to reach 0.1 ppm SO_2									
Before					66.4	0.237	ND	0.134	ND
After	88.9	101	75.8	98.9	71.3	0.270	ND	0.137	ND
Difference					4.9	0.033		0.003	

(Continued)

TABLE 3.3. (Continued)

	Residue Weights (mg)			IC Results (mg)[a]		Impinger Concentrations (mg/ml)			
	Untreated	NH_4OH Treated	NH_4OH[b] Corrected	as NH_3 salt	$SO_4^=$	$SO_4^=$	$SO_3^=$	Cl	NO_3^-
Run I: Coal-fired boiler - Required 45-minute N_2 purge to reach 0.16 ppm SO_2									
Before					75.9	0.306	ND	0.500	0.0050
After	137	138	112	103	74.0	0.319	ND	0.490	0.0050
Difference					-1.9	0.013		0.010	
Run J: Coal-fired boiler sample (pH 2) - No purge conducted									
Before					93.9	0.301	ND	0.486	0.0056
After	not analyzed			131	94.4	0.319	CP[e]	0.577	0.0062
Difference					0.5	0.018		0.091	
Run K: Wood-fired boiler sample (pH 4) - No purge conducted									
Before					1.4	0.0065	ND	IP[f]	0.0027
After	not analyzed			4.3	3.1	0.0151	0.0264	IP	0.0026
Difference					1.7	0.0086			

[a] $SO_4^=$ was determined from IC results and $SO_4^=$ as the NH_3 salt was calculated from the $SO_4^=$ IC value multiplied by the empirical correction factor, 1.375.

[b] The NH_4OH corrected residue weight is the uncorrected weight minus the NH_3 retained in the residue based on empirical calculations from the IC $SO_4^=$ results.

[c] The IC conditions for the analysis of $SO_3^=$, as formaldehyde bisulfite, were not capable of resolving the formaldehyde bisulfite from the large amount of Cl^- present in the samples.

[d] Samples preserved with propionaldehyde, with the propionaldedyde bisulfite being resolved from the Cl^- and NO_3^-.

[e] Compound present, but large Cl^- peak prevented quantification.

[f] Interfering peak present. Suspected native formaldehyde bisulfite present.

Sample runs B, C, E, and F showed that most of the SO_2 was removed from the samples. Run H showed an increase of 4.9 mg of SO_2, which is about 6 percent of the sample weight. The RDF incinerator sample was the only sample that had a significant increase and there is no explanation.

For all combustion source samples, the SO_2 in the impinger sample was removed within 60 minutes by purging with N_2 at a rate of 20 liters/min. Based on this, Method 202 specifies a 60-minute sample purge time.

The residue weights represent both samples that were untreated and treated with NH_4OH. The weights for the untreated samples was expected to be greater than the corrected values for the treated samples because of the moisture collected by the H_2SO_4. Later, it was discovered that a significant amount of Cl^- was being retained in the treated samples (by the addition of NH_4OH), whereas the HCl evaporated from the untreated samples. Therefore, no direct comparisons between the untreated and treated weights could be made. The IC analysis showed that the Cl^- concentration was equal to or greater than the $SO_4^=$ concentration in the majority of cases. The HCl that reacted with NH_4OH remained in the sample residue after the sample was taken to dryness and was counted as part of the condensible emissions.

Since HCl emissions are not considered condensibles, an experiment was designed to determine if the HCl could be removed from the sample by initially taking the aqueous inorganic fraction to dryness, resuspending this residue with deionized (DI) water, and then adding the NH_4OH to stabilize the $SO_4^=$. The results of this experiment are shown in Table 3.4. A water blank and the aqueous inorganic fraction of five impinger samples were used. A 5-ml aliquot was taken from each aqueous sample for IC analysis of $SO_4^=$ and Cl^-. Each sample was then taken to dryness and the residue resuspended in 100 ml of DI water. At this point, another 5-ml aliquot was taken for IC analysis. The sample was again taken to dryness and resuspended in 95 ml of DI water.

For coal-fired boilers (Runs C, E, and F) and the wood waste boiler (Run B), the initial heating and drying appeared to effectively remove the Cl^-. For the wood boiler, very little of the Cl^- were removed. Ammonia was suspected to be present in this sample.

The results in Table 3.4 also showed a decrease in $SO_4^=$. This was attributed to incomplete resuspension of the residue. When the samples were taken to dryness, a black film formed on the bottom of the beaker. Much of this material could not be resuspended in the DI water and, hence, the anion analysis was considered to yield low results.

Because of the uncertainty introduced by not being able to redissolve the dried residue, it was decided to repeat the experiment. For the second experiment, aliquots from the air purge experiment were used; one fraction of the aqueous sample was treated with NH_4OH and the other fraction was not treated. The samples were then taken to dryness, resuspended in water, and analyzed for Cl^- and $SO_4^=$. The results for the four samples analyzed in this experiment are presented in Table 3.5.

TABLE 3.4. EVALUATION OF Cl^- AND $SO_4^=$ LOSS ON EVAPORATION OF AQUEOUS MATRIX

Run	Sample Description	Cl^- Catch (mg)	SO_4 Catch (mg)
	DI H_2O Control Sample		
A	Before drying[a]	0.0	0.0
	After initial drying[b]	0.0	0.0
	After final drying[c]	0.0	0.1
	Method 5 Impinger Sample from Wood Waste Boiler		
B	Before drying	0.9	3.0
	After initial drying[d]	0.1	0.8
	After final drying[d]	0.1	0.9
	Combined Method 5 Impinger Sample from Wood and Coal Boiler		
C	Before initial drying	11.5	32.9
	After initial drying[d]	0.0	26.9
	After final drying[d]	0.0	26.4
	Method 5 Impinger Sample from Wood Boiler		
D	Before initial drying	14.1	2.8
	After initial drying	11.3	2.9
	After final drying	10.4	4.0
	Method 5 Impinger Sample from Coal Boiler		
E	Before initial drying	84.3	82.2
	After initial drying	0.1	57.3
	After final drying	0.1	56.1
	Method 5 Impinger Sample from Coal Boi er		
F	Before initial drying	75.2	228.4
	After initial drying	0.7	208.7
	After final drying	1.2	125.7

[a] Aliquot of 200 ml sample taken before drying without NH_4OH.
[b] Sample redissolved and aliquot taken for analysis. Remaining solution taken to dryness with NH_4OH.
[c] NH_4 OH-treated residue redissolved and aliquot taken for analysis.
[d] Did not completely redissolve.

TABLE 3.5. EVALUATION OF Cl^- AND $SO_4^=$ LOSS ON EVAPORATION OF AQUEOUS MATRIX

Run	Sample Description	Cl^- Catch (mg)	$SO_4^=$ Catch (mg)
	Sample "O" from Coal Boiler		
A	After SO_2 & Air Purging	14.5	191.1
	Untreated	0.1	81.3
	Treated	4.8	78.6
	Sample "K" from Wood Boiler		
B	After SO_2 & Air Purging	10.4	39.2
	Untreated	2.5	51.7
	Treated	6.1	49.2
	Sample "L" from Coal Boiler		
C	After SO_2 & Air Purging	71.4	70.2
	Untreated	1.3	60.5
	Treated	8.0	57.9
	Sample "N" from Coal Boiler		
D	After SO_2 & Air Purging	61.0	147.0
	Untreated	0.0	164.5
	Treated	44.4	149.3

The comparison of the treated and untreated samples shows that heating and drying effectively removed the Cl^- from the coal-fired boiler samples (Runs A, C, and D). The treated samples contained more Cl^- in the resuspended residue solution than in the untreated samples. The untreated wood-fired boiler sample (Run B) showed a significant reduction in Cl^- after drying, but the procedure still did not totally eliminate the Cl^-, which indicated that the Cl^- were not HCl, but perhaps NH_4Cl. The results also indicated that some of the NH_4Cl are lost during the drying process. The $SO_4^=$ results for the treated coal-fired boiler samples were similar to those of the previous experiment in that all of the $SO_4^=$ could not be recovered. The wood-fired boiler and untreated sample of Run D showed unexplainable increases in $SO_4^=$..

It was concluded that the HCl in the sample could be effectively removed unless the emissions also contained a significant amount of ammonia which could react with the sample during collection. The modified sample preparation procedure which involves initially taking the sample to dryness, resuspending the residue with DI water, and then adding the NH_4OH, was added to the candidate protocol.

Since a posttest purge with N_2 lasting 60 minutes at a rate of 20 liters/min would require the tester to bring a full-sized N_2 cylinder to the field, an air purge was evaluated. As shown in Table 3.6, eight samples and a DI water blank were prepared and analyzed in the same manner as described previously for the N_2 purge samples. After the samples were saturated with SO_2, they were purged with air. The results were again very much pH dependent. At pHs greater than approximately 4, SO_2 was not effectively removed. At low pHs, the data showed considerable scatter, much more than the N_2 purge. Because of the scatter in the data and because air purging could introduce the potential for oxidation of sample constituents, the N_2 purge was adopted as the procedure of choice. The air purge is offered as an option in the candidate protocol, with a warning that it has been shown to be less effective.

Just before the field evaluation of the candidate protocol, determining the amount of NH_4OH added to the sample by titration was tried. The data are not presented, but indicated that the titration technique was possible. Therefore, the technique was evaluated with field samples.

To determine the magnitude of the N_2 purge under field conditions, staff from EMB conducted paired-train testing at a coal-fired boiler burning coal with a sulfur content of about 1.5 percent. At the conclusion of each test run, one train was purged with N_2 for 60 minutes at a rate of 20 liters/min and the other train was not purged. Aliquots were taken for $SO_4^=$ analysis before evaporation and drying. The results of the paired-train testing are presented in Table 3.7.

The total CPM measured by the purged train averaged 4.7 mg, while that measured by the unpurged trains averaged 51.4 mg. For this test series, the $SO_4^=$ constituted approximately three-fourths of the CPM emissions. The residue was resuspended in water and analyzed for $SO_4^=$ and Cl^-. This initial field evaluation, conducted under the laboratory phase, clearly demonstrated

TABLE 3.6. AIR PURGE EXPERIMENTS TO DETERMINE REMOVAL OF SO_3^*

Sample ID	Process Type	Initial Sulfate (mg)	Post Purge Sulfate (mg)	Difference (mg)
O	Coal boiler	202.9	191.1	-11.8[a]
K	Wood boiler	1.9	39.2	37.3[b]
L	Coal boiler	61.2	70.2	8.0[a]
N	Coal boiler	176.2	147.0	-29.2[a]
Q	Oil boiler	8.1	22.5	14.4[a]
Q	Oil boiler	8.2	8.8	0.6[a]
R	Oil boiler	144.4	128.0	-16.4[a]
S	Oil boiler	51.2	41.5	- 9.7[a]
	DI water	0.0	53.8	53.8[b]

[a]Sample had a low pH prior to the addition of SO_2.
[b]Sample had a neutral pH prior to the addition of SO_2.

Conclusions: For all samples that had a low pH (with the exception of the first run of sample Q), the SO_2 was removed within the measurement error. For the two samples that had a neutral pH, the SO_2 was not removed quickly at the start of the purge; this apparently resulted in the SO_3^* being converted to sulfate.

TABLE 3.7. SUMMARY OF EMB TESTS CONDUCTED NOVEMBER 17-18, 1988 AT A COAL-FIRED BOILER

Sample ID	Purged	Inorganic Uncorrected (mg)	Inorganic Corrected (mg)	Organics (mg)	Total Conden (mg)	Residue (mg)					
						$SO_4^=$	$(NH_4)_2SO_4$	Cl^-	NH_4Cl	Total Corrected	Total Uncorrected
1A	No	66.8	50.2	0	50.2	44.3	60.9	0.4	0.5	44.7	61.4
1B	Yes	6.7	4.5	0	4.5	5.8	8.0	0.1	0.1	5.9	8.1
2A	No	65.0	48.6	0	48.6	43.6	60.0	0.5	0.7	44.1	60.7
2B	Yes	5.9	4.5	0	4.5	3.8	5.2	0.5	0.7	4.3	5.9
3A	No	73.1	55.4	0	55.4	47.2	64.9	2.3	3.1	49.5	68.0
3B	Yes	7.1	5.0	0	5.0	5.5	7.6	0.2	0.3	5.7	7.9
Avg. 1, 2, 3	No	68.3	51.4	0	51.4	45.0	61.9	1.1	2.2	46.1	64.1
Avg. 1, 2, 3	Yes	6.6	4.7	0	4.7	5.0	6.9	0.3	0.4	5.3	7.3

the effectiveness of the posttest N_2 purge in removing SO_2 from the impinger solution.

4.0 FIELD EVALUATION TEST 1

The first field evaluation test program was conducted at a coal-fired boiler burning 2 percent sulfur coal. Based on an EPA test report of a similar facility, the emissions were expected to have sufficient quantities of inorganic CPM.

The primary purpose of the first field test was to evaluate the revised method at a source with high inorganic CPM. Specific objectives were to: (1) determine the precision for the combined sampling and analysis procedures, (2) evaluate the effect of the posttest N_2 purge in the field, (3) evaluate the effect of heating the aqueous (inorganic) fraction in removing Cl^-, and (4) compare the $SO_4^=$ content of the inorganic fraction as determined by IC versus NH_4OH titration.

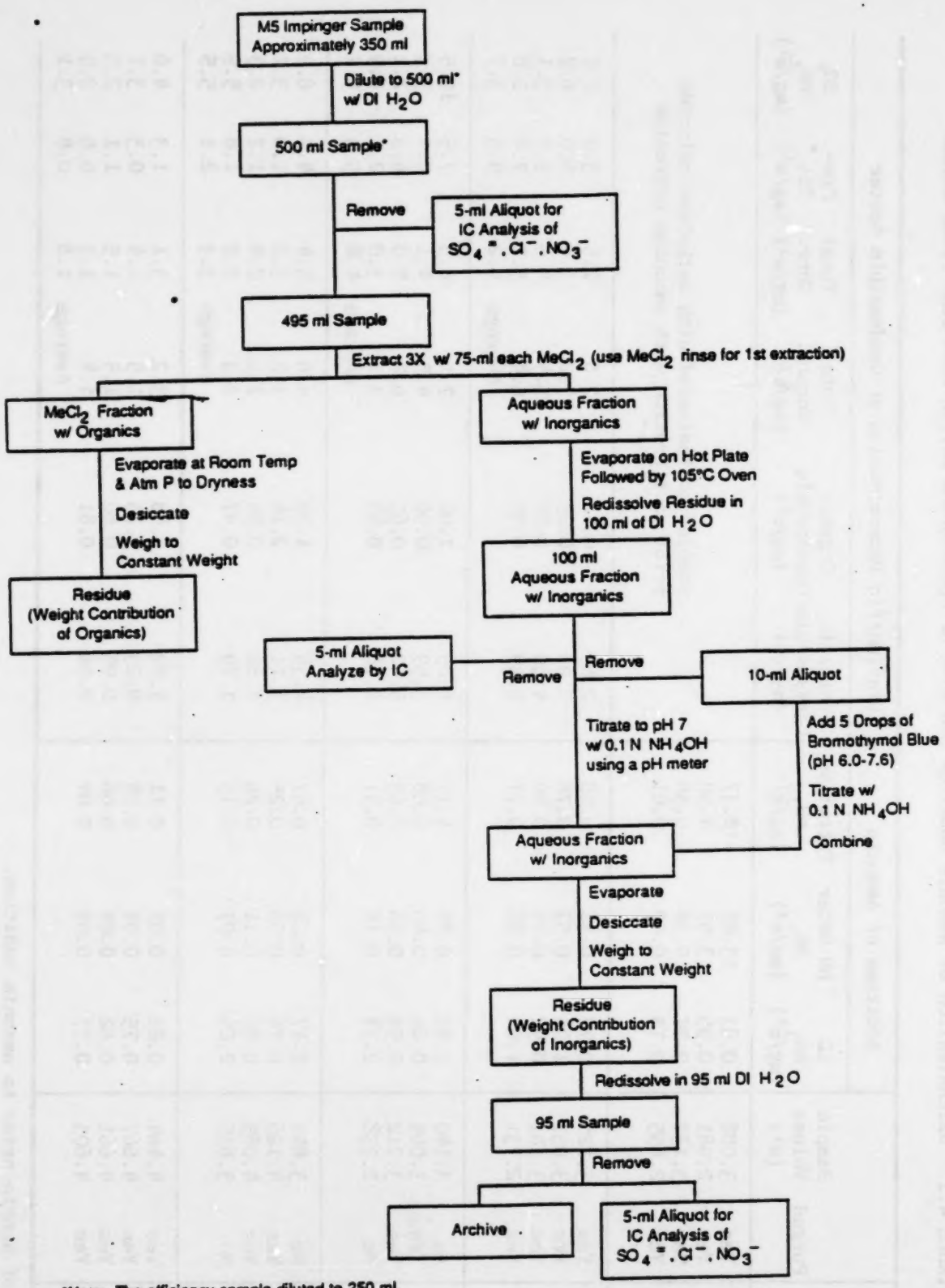
The sampling and analytical procedures used are detailed in the draft method in Appendix A. Five quadruplicate train (quad-train) runs were conducted. Sampling time was 2 hours, followed by a N_2 purge at 20 liters/min for 1 hour. In two of the runs, two of the trains (B and C) were purged to measure the effectiveness of the purge method. In the other three runs, all four trains (A, B, C, and D) were purged to assess the precision of the purge method. The samples were prepared and analyzed as shown in Figure 4.1. The results are presented in Tables 4.1 and 4.2.

Excluding results for the unpurged samples because the inorganic fraction weights ($SO_4^=$) were shown to be significantly different from those for the purged samples, the standard deviation for the sampling and analytical protocol averaged 1.1 mg/m_3 for an average stack concentration of CPM of 3.5 mg/m^3.

The $SO_4^=$ concentration (see Runs 5 and 6 in Table 4.2) in the purged samples was compared to that in the corresponding unpurged quad-train samples using Student's "t" test and the null hypothesis (see Appendix B). The $SO_4^=$ concentrations in the unpurged samples were significantly higher than that in the purged samples at the 95 percent confidence level. The $SO_4^=$ concentration results (Table 4.2) were higher than theoretically possible when compared to the inorganic CPM weight (Table 4.1); therefore, the t-test was considered invalid.

The IC analyses (Table 4.2) of sample aliquots taken initially, after the initial drying (pretitration), and after titration using NH_4OH (final drying) show that the Cl^- concentration was reduced from a level of approximately 100 mg/m^3 to a level of about 0.02 mg/m^3 by drying the sample at 105°C before adding NH_4OH, which supported the previous laboratory results (see Table 3.4).

The results of the titration techniques for ammonia determination did not agree as well as they had in the laboratory evaluation. The average ammonia values for the coal-fired boiler samples were 0.95 mg/m^3 by IC, 0.67 mg/m^3 by titration using an endpoint indicator, and 0.41 mg/m^3 by titration using a pH meter. The results of the IC analyses for $SO_4^=$ were determined to be in error and were not used to make the NH_4^- correction.



*Note: The efficiency sample diluted to 250 ml.

Figure 4.1. Scheme for preparation and analysis of impinger samples.

TABLE 4.1. DETERMINATION OF AMMONIA ADDITION AND MASS OF CONDENSIBLE MATTER FROM COAL-FIRED BOILER

Sample ID	Purged	Sample Volume (m^3)	Addition of Ammonia: IC NH_3 (mg/m^3)	Addition of Ammonia: pH Meter NH_3 (mg/m^3)	Addition of Ammonia: Titration NH_3 (mg/m^3)	Gravimetric Determination of Condensible Matter: Inorganic Condensible (mg/m^3)	Organic Condensible (mg/m^3)	Total Uncorr. (mg/m^3)	Total Corr. (mg/m^3)	Pre-Tit.* (mg/m^3)	SO_4 +NO_3 (mg/m^3)
3-A	Yes	3.088	0.83	13.05	18.37						
3-B	Yes	2.981	0.95	3.97	4.30						
3-C	Yes	3.137	0.77	0.36	0.36	Samples contaminated with methylene chloride prior to titration with ammonium hydroxide					
3-D	Yes	2.655	0.73	0.40	0.61						
4-A	Yes	3.120	0.72	0.31	0.58	2.65	0.12	2.8	2.5	3.2	2.8
4-B	Yes	3.037	1.94	0.53	0.78	3.93	0.25	4.2	3.6	5.0	6.2
4-C	Yes	3.181	0.92	0.45	0.60	4.60	0.79	5.4	4.9	5.7	3.1
4-D	Yes	2.731	1.04	0.68	0.77	5.99	0.37	6.4	5.7	7.4	2.8
								Average	4.2	5.3	3.7
5-A	No	3.140	3.62	0.84	1.12	6.05	1.08	7.1	6.3	7.5	10.5
5-B	Yes	3.065	0.86	0.40	0.68	3.59	0.90	4.5	4.1	5.1	3.3
5-C	Yes	3.212	0.59	0.36	0.65	5.52	0.65	6.2	5.8	6.3	2.2
5-D	No	2.738	2.74	0.18	0.31	2.66	0.48	3.1	3.0	2.1	6.9
								Average	4.8	5.3	5.7
6-A	No	3.841	2.47	0.28	0.47	4.34	1.29	5.6	5.4	4.3	8.9
6-B	Yes	4.126	0.76	0.08	0.25	1.11	2.14	3.2	3.2	1.0	3.2
6-C	Yes	4.085	0.85	0.11	0.26	1.66	0.85	2.5	2.4	1.2	2.9
6-D	No	3.835	2.05	0.07	0.15	1.79	0.47	2.3	2.2	1.8	5.9
								Average	3.3	2.1	5.5
7-A	Yes	4.464	0.81	0.07	0.11	1.72	1.48	3.2	3.1	1.3	4.6
7-B	Yes	4.667	0.75	0.04	0.04	0.23	1.23	1.5	1.4	0.3	3.1
7-C	Yes	4.661	0.62	0.09	0.06	0.95	0.60	1.5	1.5	1.1	2.3
7-D	Yes	4.603	0.77	0.07	0.04	0.56	0.81	1.4	1.3	0.5	2.5
								Average	1.8	0.8	3.1

*Weight of sample prior to ammonia addition.

TABLE 4.2. ION CHROMATOGRAPHIC RESULTS FOR THE SULFATE, CHLORIDE, AND NITRATE, IN COAL-FIRED BOILER SAMPLES

Sample ID	Purged	Initial			After Initial Drying and Redissolution			After Final Drying and Redissolution		
		Sulfate (mg/m^3)	Chloride (mg/m^3)	Nitrate (mg/m^3)	Sulfate (mg/m^3)	Chloride (mg/m^3)	Nitrate (mg/m^3)	Sulfate (mg/m^3)	Chloride (mg/m^3)	Nitrate (mg/m^3)
3-A	Yes	2.21	70.32	1.04	1.41	30.11	0.38	0.31	29.75	0.21
3-B	Yes	2.53	74.36	1.18	1.27	7.94	0.22	0.74	7.73	0.23
3-C	Yes	2.06	76.75	0.20	1.37	0.00	0.00	1.33	0.02	0.00
3-D	Yes	1.94	80.66	0.00	1.46	0.01	0.00	1.42	0.01	0.00
4-A	Yes	1.93	26.15	0.98	1.04	0.01	0.02	1.05	0.02	0.02
4-B	Yes	5.18	87.08	1.22	1.78	0.02	0.01	1.61	0.02	0.01
4-C	Yes	2.46	86.93	0.83	1.38	0.01	0.00	1.42	0.01	0.00
4-D	Yes	2.76	99.68	0.23	2.24	0.02	0.00	2.20	0.00	0.00
5-A	No	9.66	84.96	1.46	3.26	0.01	0.02	3.10	0.01	0.02
5-B	Yes	2.30	97.96	1.11	1.28	0.02	0.01	1.17	0.02	0.01
5-C	Yes	1.56	88.38	0.77	1.08	0.02	0.00	1.02	0.02	0.00
5-D	No	7.31	74.79	0.00	0.78	0.01	0.00	0.75	0.01	0.00
6-A	No	6.58	127.6	2.46	1.01	0.01	0.02	1.01	0.01	0.02
6-B	Yes	2.02	127.4	1.22	0.31	0.02	0.01	0.32	0.01	0.01
6-C	Yes	2.26	124.6	0.69	0.46	0.01	0.00	0.47	0.01	0.00
6-D	No	5.46	122.2	0.42	0.35	0.01	0.00	0.35	0.01	0.00
7-A	Yes	2.17	116.0	2.46	0.31	0.01	0.01	0.30	0.01	0.01
7-B	Yes	2.00	117.0	1.10	0.13	0.02	0.01	0.13	0.01	0.01
7-C	Yes	1.65	97.3	0.63	0.33	0.00	0.00	0.32	0.00	0.00
7-D	Yes	2.04	117.3	0.47	0.26	0.01	0.00	0.29	0.01	0.00

To determine if the N_2 purge was removing any of the organic matter, the organic condensible results were compared for the purged and unpurged sample pairs from quad-train Runs 5 and 6. The results shown in Table 4.1 indicate that the organic values for the purged and unpurged samples were equivalent at the 95% confidence level. Therefore, the N_2 purge did not affect the concentrations of the organic condensibles measured.

CONCLUSIONS

The results of the first field test (see Tables 4.1 and 4.2) indicated that a coal-fired boiler with significantly greater emissions was needed to adequately determine the precision of the combined sampling and analysis protocol. The posttest N_2 purge and the pretitration drying of aqueous samples proved to be effective. Without removal of the dissolved SO_2 by purging and the HCl by heating, the CPM measured for the average sample would have been about 120 mg/m^3 instead of the actual value of about 4 mg/m^3. Since the total CPM results were much lower than had originally been anticipated, comparison of the IC results with the gravimetric determinations was not as close as had been expected. An additional evaluation at an emission source with high $SO_4^=$ levels was recommended to provide a more accurate comparison of the measured values.

5.0 FIELD EVALUATION TEST 2

The second field evaluation was conducted at a wood-fired boiler. The sampling location was after an electrified fabric filter. Based on previous tests at a similar facility, the emissions were expected to have sufficient quantities of organic CPM.

The primary purpose of this field test was to evaluate the revised method at a site high in organic CPM emissions. Specific objectives were to: (1) determine the precision, (2) evaluate the effectiveness of the posttest N_2 purge, and (3) evaluate the effectiveness of heating the aqueous (inorganic) fraction in removing Cl^-.

The sampling and analytical procedures used are detailed in the draft method reproduced in Appendix A. Five two-hour quad-train runs were performed, followed by a one-hour N_2 purge of the impinger trains at 20 liters/min. In two of the runs, two or three of the trains were purged. In the other three runs, all four trains were purged. The samples were prepared and analyzed in the same manner as the samples from the first field evaluation (see Figure 4.1), except only an initial anion analysis was made.

The results of the test are shown in Table 5.1. As seen, the $SO_4^=$ concentration was near the limit of detection (<0.07 mg/m^3), and thus, the N_2 purge would not have been necessary. The results showed that N_2 purging did not adversely affect the organic CPM determinations; the mass of CPM was the same for the purged and unpurged samples.

Since the organic CPM was shown to be the same for the purged and unpurged samples, all samples were used to calculate the precision of the method, which turned out to be 13.0 ± 2.1 mg/m^3.

The results of the IC and titration techniques for ammonia determination did not agree as well as they did in the laboratory evaluation. The average calculated ammonia values (see Table 5.2) were 0.03 mg/m^3 by IC and 0.32 mg/m^3 by titration. However, this difference is not significant when compared to typical particulate concentration levels of 30 to 50 mg/m^3 for a compliance determination.

CONCLUSIONS

The results of the second field evaluation at a wood-fired boiler led to several conclusions and recommendations. A N_2 purge conducted at a rate of 20 liters/min for 60 minutes at the end of a test run does not significantly affect the determination of organic or inorganic CPM when SO_2 emission levels are near detection limit or are very low. Therefore, it would be acceptable to omit the purge at sources not expected to have significant concentrations of SO_2 (an incorrect judgement may cause a positive bias). If the sample pH is greater than 4.5, indicating low concentrations of H_2SO_4 and SO_2 in the sample, the ammonia addition is no longer required to stabilize the $SO_4^=$.

TABLE 5.1. DETERMINATION OF AMMONIA ADDITION AND MASS OF CONDENSIBLE MATTER FROM WOOD-FIRED BOILER

Sample ID	Purged	Sample Volume (m^3)	Ammonia Added in Titration (IC) (mg/m^3)	Ammonia Added in Titration (pH Meter) (mg/m^3)	Gravimetric Determination of Condensible Matter			
					Inorganic Condensible (mg/m^3)	Organic Condensible (mg/m^3)	Total Uncorr. (mg/m^3)	Total Corr. (mg/m^3)
8-A	Yes	1.661	0.02	0.22	2.52	2.85	5.4	5.4
8-B	Yes	1.586	0.02	0.14	2.72	6.81	9.5	9.5
8-C	No	1.518	0.02	0.18	3.11	4.19	7.4	7.4
8-D	No	1.378	0.02	0.23	2.55	9.67	12.2	12.2
						Average	8.6	8.6
9-A	Yes	1.614	0.03	0.14	7.42	8.12	15.5	15.5
9-B	Yes	1.625	0.02	0.31	6.87	13.79	20.5	20.5
9-C	Yes	1.477	0.02	0.23	4.92	12.08	17.0	17.0
9-D	Yes	1.528	0.02	0.24	7.14	13.79	21.0	21.0
						Average	18.5	18.5
10-A	No	1.666	0.04	0.13	2.78	5.73	8.5	8.5
10-B	Yes	1.677	0.02	0.22	2.98	4.92	7.9	7.9
10-C	No	1.555	0.02	0.12	2.77	6.25	9.0	9.0
10-D	No	1.622	0.02	0.11	3.34	4.30	7.6	7.6
						Average	8.3	8.3
11-A	Yes	1.353	0.03	0.17	5.68	6.73	12.4	12.4
11-B	Yes	0.814	0.04	0.94	9.42	5.09	14.5	14.5
11-C	Yes	1.332	0.03	0.56	5.87	6.26	12.1	12.1
11-D	Yes	1.359	0.03	0.17	3.43	11.62	15.1	15.1
						Average	13.3	13.3
12-A	Yes	0.686	0.05	0.46	5.34	4.65	10.0	10.0
12-B	Yes	0.935	0.04	0.73	8.86	9.50	18.4	18.4
12-C	Yes	0.857	0.04	0.69	6.72	12.50	19.2	19.2
12-D	Yes	0.864	0.05	0.26	6.22	13.00	19.2	19.2
						Average	16.7	16.7

*Corrections based on IC data for ammonia.

TABLE 5.2. WOOD-FIRED BOILER ION CHROMATOGRAPHIC RESULTS FOR SULFATE AND CHLORIDE

Sample ID	Purged	Initial	
		Sulfate (mg/m^3)	Chloride (mg/m^3)
8-A	Yes	0.06	1.11
8-B	Yes	0.06	1.19
8-C	No	0.06	1.44
8-D	No	0.06	1.44
9-A	Yes	0.09	0.06
9-B	Yes	0.06	0.06
9-C	Yes	0.06	0.76
9-D	Yes	0.06	0.06
10-A	No	0.10	1.21
10-B	Yes	0.06	1.09
10-C	No	0.06	1.23
10-D	No	0.06	0.06
11-A	Yes	0.07	1.29
11-B	Yes	0.11	1.92
11-C	Yes	0.07	0.07
11-D	Yes	0.07	0.07
12-A	Yes	0.13	0.13
12-B	Yes	0.10	2.62
12-C	Yes	0.11	2.32
12-D	Yes	0.14	2.12

In conclusion, the evaluation of the draft sampling and analytical protocol at a wood-fired boiler demonstrated adequate precision. The modifications for testing at sources with low SO_2 emissions involving elimination of (1) the posttest purge and (2) addition of the NH_4OH when the sample pH is greater than 4.5 were added to the draft protocol.

6.0 FIELD EVALUATION TEST 3

Because the first coal-fired boiler tested did not have sufficient SO_3 emissions, the revised test method was evaluated at a second coal-fired boiler with SO_2 levels in excess of 2000 ppm.

The objectives of the second coal-fired boiler field test were to (1) determine the precision of the draft method, (2) evaluate the effectiveness of the initial sample drying step to remove Cl^-, (3) compare the two procedures (IC analysis and titrimetric) of determining the amount of ammonia added to the sample, (4) determine the effect of the posttest purge, and (5) determine the collection efficiency of the impinger for CPM.

The sampling and analytical procedures followed those described in Appendix A and depicted in Figure 4.1, with the following modifications:

- Initial dilution of the impinger sample plus water rinse was to 800 ml, due to the high moisture content of the sample gas.
- The first $MeCl_2$ extraction was performed using the $MeCl_2$ rinse catch.
- The two remaining $MeCl_2$ extractions were performed with 50 ml each of fresh $MeCl_2$.
- After redissolving the residue in 100 ml of DI H_2O, only the 5-ml aliquot for IC analysis was removed. The NH_4OH/bromothymol blue titration was rejected in favor of a single NH_4OH titration of the remaining 95-ml sample to pH 7.0 using a pH meter.
- After evaporating and desiccating of the titrated inorganic samples, final weights were recorded and the samples were archived for further analysis.

The quad-train run scheme was almost identical to that for the two previous field tests. Run times were two hours, followed by a 60-minute N_2 purge of the impinger trains at 20 liters/min. Train A in each quad-train run was fitted with an extra impinger before the silica gel impinger. The catches from each of these impingers were kept separate for the impinger efficiency evaluations. In two of the quad-train runs, only two of the trains were purged with N_2. For the remaining runs, all four trains were purged with N_2.

Tables 6.1 and 6.2 present the results of the third field evaluation. The average concentrations for the gravimetric analysis of the total CPM ranged from 25 mg/m^3 to 48 mg/m^3 with standard deviations ranging from ± 7.3 to $\pm$ 9.9 mg/m^3. The effect of the N_2 purge on the $SO_4^=$ concentrations was evident. In the initial IC aliquots, before heating, the purged train $SO_4^=$ concentrations ranged from 1.7 mg/m^3 to 8.10 mg/m^3. The $SO_4^=$ concentrations for trains not purged ranged from 16.3 mg/m^3 to 25.6 mg/m^3. Thus, the $SO_3^=$ concentrations in the unpurged samples were 280% and 178% higher than the average $SO_4^=$ levels in the purged samples. These results agree with those from the laboratory evaluations and the two previous field evaluation tests

TABLE 6.1. DETERMINATION OF AMMONIA ADDITION AND MASS OF CONDENSIBLE PARTICULATE MATTER FROM COAL-FIRED BOILER

Sample ID	Purged	Sample Volume (m^3)	Addition of Ammonia: IC NH_3 (mg/m^3)	Addition of Ammonia: ph Meter NH_3 (mg/m^3)	Determination of Condensible Particulate: Inorganic Condensible (mg/m^3)	Organic Condensible (mg/m^3)	Total Uncorr. (mg/m^3)	Total Corr. (mg/m^3)
1a	Yes		(Sample blown out of		out of impinger during purge)			
Extra impinger			(0.37)	(0.0)	3.9	0.3	4.2	(4.2)
1b	Yes	2.335	*3.04	4.20	43.1	0.5	43.6	40.6
1c	No	2.299	7.31	4.37	43.2	0.3	43.5	36.2
1d	No	2.307	9.60	9.37	45.7	1.9	47.6	38.0
Average			6.65	6.0				
2a	Yes	2.453	1.73	2.73	38.8	0.3	39.1	37.4
2b	Yes	2.480	1.84	3.60	39.4	0.6	40.0	38.2
2c	No	2.487	6.11	4.12	44.2	1.4	45.6	39.5
2d	No		(Sample taken to dry		ness on hot plate during dry down)			
Average			3.2	3.5				
3a	Yes	2.507	2.18	4.54	44.6	2.5	47.1	44.9
Extra impinger			(0.43)	(0.0)	5.9	2.7	8.6	(8.6)
3b	Yes		(Sand got in sample		during dry down)			
3c	Yes	2.538	1.50	2.97	25.5	1.2	26.8	25.2
3d	Yes	2.542	0.64	1.94	35.8	1.2	37.0	36.4
Average			1.44	3.2				35.5 ± 9.9
4a	Yes	2.476	0.64	1.89	30.1	0.3	30.4	29.8
4b	Yes	2.519	0.79	2.12	46.2	0.4	46.6	45.8
4c	Yes	2.492	1.20	2.30	49.0	5.0	54.0	52.8
4d	Yes	2.514	1.99	2.93	47.5	0.5	48.0	46.0
Average			1.2	2.3				43.6 ± 9.8
5a	Yes	2.491	2.06	8.35*	49.4	0.4	49.8	47.7
Extra impinger			(1.19)	(0.0)	3.5	0.0	3.5	(3.5)
5b	Yes	2.537	2.48	2.45	39.5	0.3	39.8	37.3
5c	Yes	2.516	0.83	1.79	33.3	1.1	34.4	33.6
5d	Yes		(Large leak in		sample train)			
Average			1.8	4.2(2.1)				39.5 ± 7.3

*Sample showed chloride contamination (see Table 6.2).

TABLE 6.2. ION CHROMATOGRAPHIC RESULTS FOR SULFATE, CHLORIDE, AND NITRATE FOR FLUE GAS SAMPLES FROM A COAL-FIRED BOILER

Sample ID	Train Purged	Initial			Pre-Titration		
		Sulfate (mg/m^3)	Chloride (mg/m^3)	Nitrate (mg/m^3)	Sulfate (mg/m^3)	Chloride (mg/m^3)	Nitrate (mg/m^3)
1-b	Yes	8.10	13.00	0.00[1]	11.88	0.00	0.00
1-c	No	19.50	11.40	0.00[1]	13.77	0.20	0.00
1-d	No	25.60	7.90	0.00[1]	19.53	0.30	0.07
2-a	Yes	4.60	8.50	0.00[1]	5.18	0.00	0.00
2-b	Yes	4.90	8.70	0.00[1]	6.41	0.20	0.80
2-c	No	16.30	8.60	0.00[1]	9.41	0.00	0.00
3-a	Yes	5.80	8.70	0.00[1]	13.03	0.00	0.00
3-c	Yes	4.00	8.70	0.00[1]	9.19	0.30	0.60
3-d	Yes	1.70	8.90	0.00[1]	5.47	0.03	0.07
4-a	Yes	1.70	10.40	0.00[1]	4.05	0.30	0.80
4-b	Yes	2.10	8.50	0.00[1]	3.60	0.30	0.70
4-c	Yes	3.20	6.40	0.80	4.27	0.30	0.50
4-d	Yes	5.30	6.40	0.50	5.83	0.00	0.00
5-a	Yes	5.50	6.40	0.70	4.94	7.10[2]	2.00
5-b	Yes	6.60	7.40	0.40	5.13	0.01	0.00
5-c	Yes	2.20	7.00	0.80	2.87	0.00	0.00
5-d	Yes	2.80	5.10	0.60	4.75	0.10	0.00
Collection Efficiency (4th) Impingers							
1-a	Yes	6.00	0.20	0.30	0.99	0.10	0.00
5-a	Yes	1.60	2.10	0.30	1.34	0.80	0.30

[1] Phosphate ion chromatographic interference.
[2] Sample contaminated.

and demonstrate further that the N_2 purge satisfactorily removes the dissolved SO_2 collected in the impingers.

In comparing the IC results for the initial Cl^- concentration to the concentration after the sample was taken to dryness (pre-titration, see Table 6.2), the effectiveness of initially taking the sample to dryness to remove Cl^- is clearly evident.

An extra impinger was placed before to the silica gel impinger in Train A of each quad-train group to determine the collection efficiency. The extra impinger collected about 10 percent of the total sample catch, which demonstrated a need for an additional impinger efficiency.

The final comparison involved determining if the amount of ammonia added to the sample could be determined by titration in lieu of IC analysis (see Appendix B for calculations). The average of the results for the two procedures were within 1 mg/m^3 for all but the last quad-train run where one of the samples was contaminated with Cl^- (see Table 6.2).

CONCLUSIONS

The procedure to remove the Cl^- by taking the sample to dryness again proved effective. The two techniques for determining the amount of ammonia added to the sample were shown to be comparable. The EPA decided that the IC technique would be shown as the procedure of choice, with the tester permitted to use the titration technique as an alternative procedure. The posttest purge was again shown to be effective and is required by the draft method when SO_2 is present in the stack emissions. The precision of the draft sampling and analytical protocol was worse than had been anticipated. The impinger train did not demonstrate sufficient collection efficiency; therefore, the train configuration was modified to include two tipped impingers and the sampling reagent (water) in the first three impingers.

7.0 REFERENCES

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9. "Sampling Condensible Emissions from Stationary Sources," Department of Environmental Quality, State of Oregon.

10. Federal Register, Vol. 53, No. 68, p. 11688, April 8, 1988.

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12. "Determination of Particulate After Removal of Sulfuric Acid and Waters of Hydration," Entropy Environmentalists Inc., internal memo.

13. DeWees, W. G., "PM_{10} Emissions from Stationary Sources - How Do We Define, Measure, Control, and Regulate Them?" Presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 1985. April 8, 1988.

APPENDIX A

Method 202 - Determination of Condensible Particulate Emissions from Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability. This method applies to the determination of condensible particulate matter (CPM) emissions from stationary sources. It is intended to represent condensible matter as material that condenses after passing through an in-stack filter (**Note:** The filter catch can be analyzed according to Method 17 procedures). This method may be used in conjunction with Method 201 or 201A if the probes are glass lined. This method may also be modified to measure material that condenses at other temperatures by specifying the filter temperature.

1.2 Principle. The CPM is collected in the impinger portion of a Method 17 (Appendix A, 40 CFR Part 60) type sampling train. The impinger contents are immediately purged after the run with nitrogen (N_2) to remove dissolved sulfur dioxide (SO_2) gases from the impinger contents. The impinger solution is then extracted with methylene chloride ($MeCl_2$). The organic and aqueous fractions are then taken to dryness and the residues weighed. The total of both fractions represents the CPM.

2. PRECISION AND INTERFERENCE

2.1 Precision. The precisions based on method development tests at a wood waste burner and two coal-fired boilers are 13.0 $\pm$ 2.1 mg/m^3, 3.5 $\pm$ 1.1 mg/m^3, and 39.5 $\pm$ 9.0 mg/m^3, respectively.

2.2 Interference. Ammonia (e.g., in sources that use ammonia injection as a control technique) interferes by reacting with the hydrogen chloride (HCl) in the gas stream to form ammonium chloride (NH_4Cl) which would be measured as CPM. The sample may be analyzed for chloride and the equivalent amount of NH_4Cl can be subtracted from the CPM weight.

3. APPARATUS

3.1 Sampling Train. Same as in Method 17, Section 2.1, with the following exceptions noted below (see Figure 202-1). **Note:** Mention of trade names or specific products does not constitute endorsement by EPA.

3.1.1 The probe extension shall be glass-lined.

3.1.2 A Teflon filter support shall be used.

3.1.3 Both the first and second impingers shall be of the Greenburg-Smith design with the standard tip.

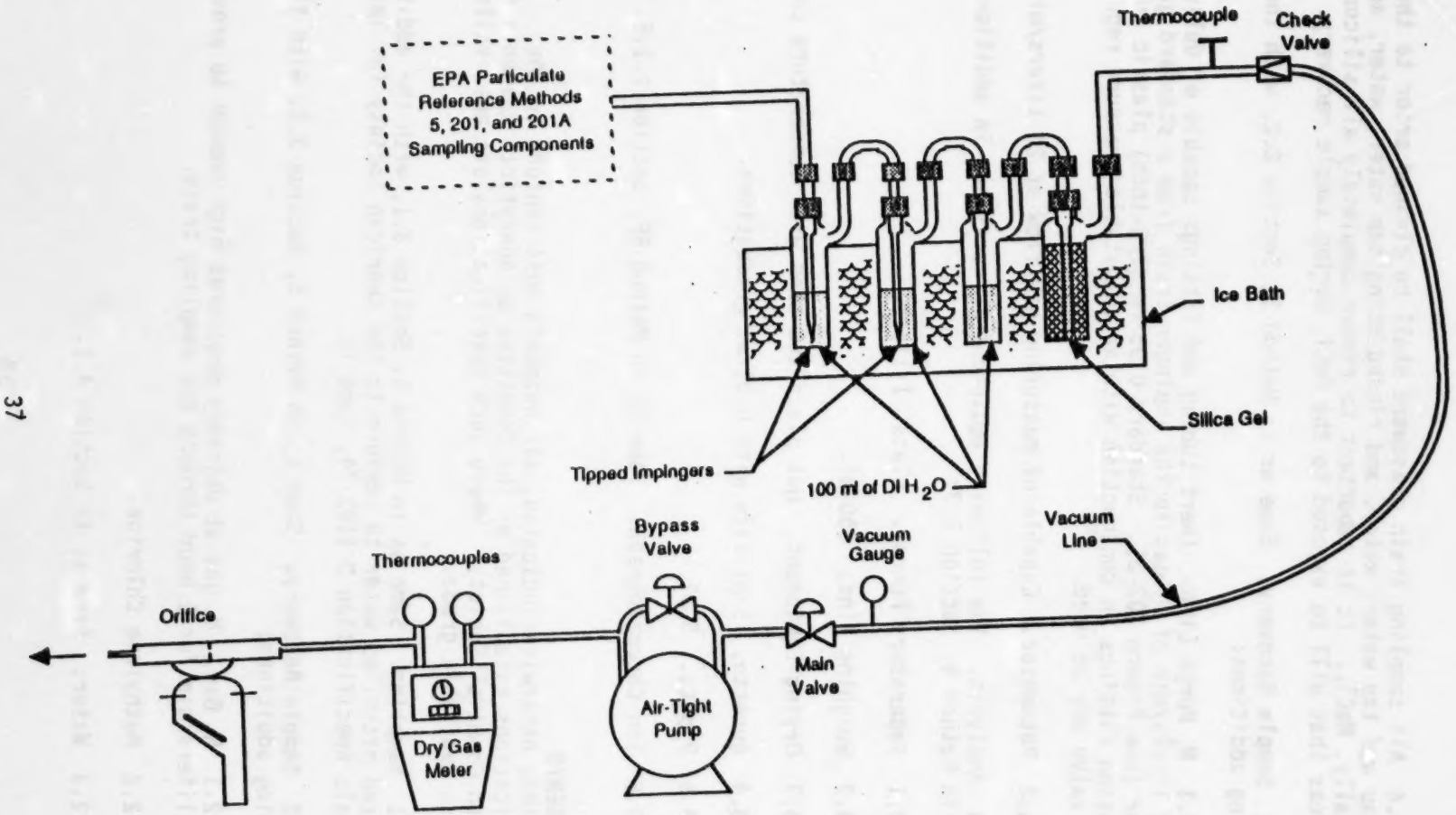

Figure 202-1. Schematic of condensible particulate sampling train.

3.1.4 All sampling train glassware shall be cleaned prior to the test with soap and tap water, water, and rinsed using tap water, water, acetone, and finally, $MeCl_2$. It is important to remove completely all silicone grease from areas that will be exposed to the $MeCl_2$ during sample recovery.

3.2 **Sample Recovery.** Same as in Method 5, Section 2.2, with the following additions:

3.2.1 **N_2 Purge Line.** Inert tubing and fittings capable of delivering 0 to 28 liters/min of N_2 gas to the impinger train from a standard gas cylinder (see Figure 202-2). Standard 0.95 cm (3/8-inch) plastic tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.

3.2.2 **Rotameter.** Capable of measuring gas flow at 20 liters/min.

3.3 **Analysis.** The following equipment is necessary in addition to that listed in Method 5, Section 2.3:

3.3.1 **Separatory Funnel.** Glass, 1-liter.

3.3.2 **Weighing Tins.** 350-ml.

3.3.3 **Drying Equipment.** Hot plate and oven with temperature control.

3.3.4 **Burette.** 5-ml size with 0.01-ml graduations.

3.3.5 **Pipets.** 5-ml.

3.3.6 **Ion Chromatograph.** Same as in Method 5F, Section 2.1.6.

4. REAGENTS

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

4.1 **Sampling.** Same as in Method 5, Section 3.1, with the addition of deionized distilled water to conform to the American Society for Testing and Materials Specification D 1193-74, Type II.

4.2 **Sample Recovery.** Same as in Method 5, Section 3.2, with the following additions:

4.2.1 **N_2 Gas.** N_2 gas at delivery pressures high enough to provide a flow of 20 liters/min for 1 hour through the sampling train.

4.2.2 **Methylene Chloride.**

4.2.3 **Water.** Same as in Section 4.1.

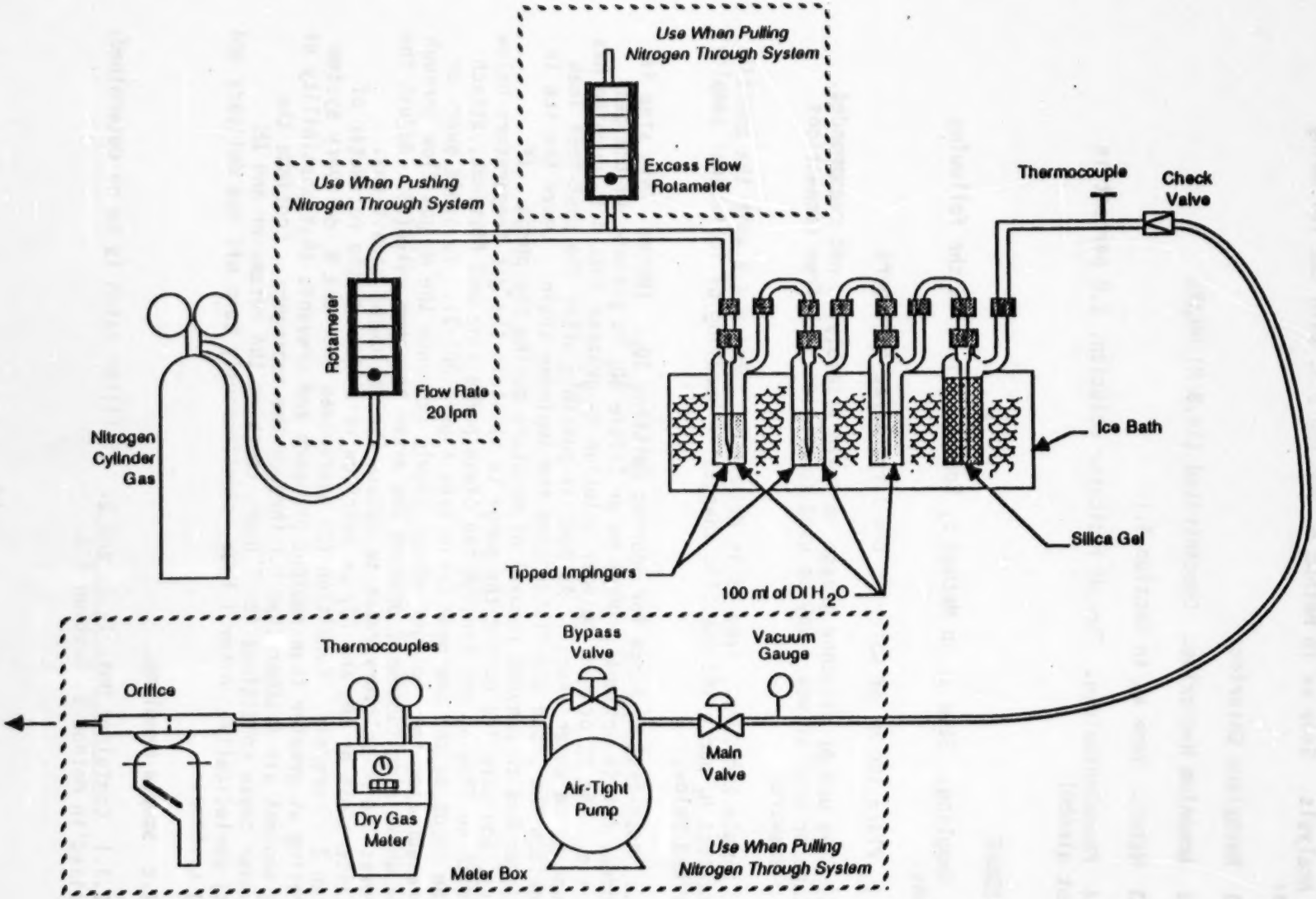

Figure 202-2. Schematic of post-test nitrogen purge system.

4.3 Analysis. Same as in Method 5, Section 3.3, with the following additions:

4.3.1 Methylene Chloride.

4.3.2 Ammonium Hydroxide. Concentrated (14.8 M) NH_4OH.

4.3.3 Water. Same as in Section 4.1.

4.3.4 Phenolphthalein. The pH indicator solution, 1.0 percent in 60 percent alcohol.

5. PROCEDURE

5.1 Sampling. Same as in Method 5, Section 4.1, with the following exceptions:

5.1.1 Place 100 ml of water in the first three impingers.

5.1.2 The use of silicone grease in train assembly is not recommended. Teflon tape or similar means may be used to provide leak-free connections between glassware.

5.2 Sample Recovery. Same as in Method 17, Section 4.2 with the addition of a post-test N_2 purge and specific changes in handling of individual samples as described below.

5.2.1 Post-test N_2 Purge for Sources Emitting SO_2. **(Note:** This step is recommended, but is optional. When no or little SO_2 is present in the gas stream, i.e., the pH of the impinger solution is greater than 4.5, purging has been found to be unnecessary.) As soon as possible after the post-test leak check, detach the probe and filter from the impinger train. Leave the ice in the impinger box to prevent removal of moisture during the purge. If necessary, add more ice during the purge to maintain the gas temperature below 20°C. With no flow of gas through the clean purge line and fittings, attach it to the input of the impinger train (see Figure 202-2). To avoid over- or under-pressurizing the impinger array, slowly commence the N_2 gas flow through the line while simultaneously opening the meter box pump valve(s). Adjust the pump bypass and N_2 delivery rates to obtain the following conditions: (1) 20 liters/min or $\Delta H_@$ and (2) an overflow rate through the rotameter of less than 2 liters/min. Condition (2) guarantees that the N_2 delivery system is operating at greater than ambient pressure and prevents that possibility of passing ambient air (rather than N_2) through the impingers. Continue the purge under these conditions for 1 hour, checking the rotameter and ΔH value(s) periodically. After 1 hour, simultaneously turn off the delivery and pumping systems.

5.2.2 Sample Handling.

5.2.2.1 Container Nos. 1, 2, and 3. If filter catch is to be determined, as detailed in Method 5, Section 4.2.

5.2.2.2 Container No. 4 (Impinger Contents). Measure the liquid in the first three impingers to within 1 ml using a clean graduated cylinder or by weighing it to within 0.5 g using a balance. Record the volume or weight of liquid present to be used to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid into a clean sample bottle (glass or plastic); rinse each impinger and the connecting glassware, including probe extension, twice with water, recover the rinse water and add it to the same sample bottle. Mark the liquid level on the bottle.

5.2.2.3 Container No. 5 ($MeCl_2$ Rinse). Follow the water rinses of each impinger and the connecting glassware, including the probe extension with two rinses of $MeCl_2$; save the rinse products in a clean, glass sample jar. Mark the liquid level on the jar.

5.2.2.4 Container No. 6 (Water Blank). Once during each field test, place 500 ml of water in a separate sample container.

5.2.2.5 Container No. 7 ($MeCl_2$ Blank). Once during each field test, place in a separate glass sample jar a volume of $MeCl_2$ approximately equivalent to the volume used to conduct the $MeCl_2$ rinse of the impingers.

5.2.2.6 Container No. 8 (Acetone Blank). As described in Method 5, Section 4.2.

5.3 Analysis. Record the data required on a sheet such as the one shown in Figure 202-3. Handle each sample container as follows:

5.3.1 Container Nos. 1, 2, and 3. If filter catch is analyzed, as detailed in Method 5, Section 4.3.

5.3.2 Container Nos. 4 and 5. Note the level of liquid in the containers and confirm on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in Container No. 4 either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Remove a 5-ml aliquot and set aside for later ion chromatographic (IC) analysis of sulfates. (Note: Do not use this aliquot to determine chlorides since the HCl will be evaporated during the first drying step; Section 8.2 details a procedure for this analysis.)

5.3.2.1 Extraction. Separate the organic fraction of the sample by adding the contents of Container No. 5 ($MeCl_2$) to the contents of Container No. 4 in a 1000-ml separatory funnel. After mixing, allow the aqueous and organic phases to fully separate, and drain off most of the organic/$MeCl_2$ phase. Then add 75 ml of $MeCl_2$ to the funnel, mix well, and drain off the lower organic phase. Repeat with another 75 ml of $MeCl_2$. This extraction should yield about 250 ml of organic extract. Each time, leave a small amount of the organic/$MeCl_2$ phase in the separatory funnel ensuring that no water is collected in the organic phase. Place the organic extract in a tared 350-ml weighing tin.

Moisture Determination

Volume or weight of liquid in impingers _____ ml or g
Weight of moisture in silica gel _____ g

Sample Preparation (Container No. 4)

Amount of liquid lost during transport _____ ml
Final volume _____ ml
pH of sample prior to analysis _____
Addition of NH_4OH required? _____
Sample extracted 2X with 75 ml $MeCl_2$? _____

For Titration of Sulfate

Normality of NH_4OH _____ N
Volume of sample titrated _____ ml
Volume of titrant _____ ml

Sample Analysis

Container number	Weight of Condensible Particulate, mg		
	Final Weight	Tare Weight	Weight Gain
4 (Inorganic) 4 & 5 (Organic)			

Total	
Less Blank	
Weight of Condensible Particulate	

Figure 202-3. Analytical data sheet.

5.3.2.2 Organic Fraction Weight Determination (Organic Phase from Container Nos. 4 and 5). Evaporate the organic extract at room temperature and pressure in a laboratory hood. Following evaporation, desiccate the organic fraction for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg.

5.3.2.3 Inorganic Fraction Weight Determination. Using a hot plate, or equivalent, evaporate the aqueous phase to approximately 50 ml; then evaporate to dryness in a 105°C oven. Redissolve the residue in 100 ml of water. Add five drops of phenolphthalein to this solution, then add concentrated (14.8 M) NH_4OH until the sample turns pink. Any excess NH_4OH will be evaporated during the drying step. Evaporate the sample to dryness in a 105°C oven, desiccate the sample for 24 hours, weigh to a constant weight, and record the results to the nearest 0.1 mg. (Note: The addition of NH_4OH is recommended, but is optional when no or little SO_2 is present in the gas stream, i.e., when the pH of the impinger solution is greater than 4.5, the addition of NH_4OH is not necessary.)

5.3.2.4 Analysis of Sulfate by IC to Determine Ammonium Ion (NH_4^-) Retained in the Sample. (Note: If NH_4OH is not added, omit this step.) Determine the amount of sulfate in the aliquot taken from Container No. 4 earlier as described in Method 5F (Appendix A, 40 CFR Part 60). Based on the IC $SO_4^=$ analysis of the aliquot, calculate the correction factor to delete the NH_4^- retained in the sample and to add the combined water removed by the acid-base reaction (see Section 7.2).

5.3.3 Analysis of Water and $MeCl_2$ Blanks (Container Nos. 6 and 7). Analyze these sample blanks as described above in Sections 5.3.2.3 and 5.3.2.2, respectively. The sum of the values for the water blank and the $MeCl_2$ blank must be less than 2 mg or 5 percent of the mass of the CPM ($m_o + m_r$), whichever is greater. If the sum of the actual blank values is greater, then subtract 2 mg or 5 percent of the mass of the CPM, whichever is greater.

5.3.4 Analysis of Acetone Blank (Container No. 8). Same as in Method 5, Section 4.3.

6. CALIBRATION

Same as in Method 5, Section 5, except calibrate the IC according to the procedures in Method 5F, Section 5.

7. CALCULATIONS

Same as in Method 5, Section 6, with the following additions:

7.1 Nomenclature. Same as in Method 5, Section 6.1 with the following additions.

C_{cpm} = Concentration of the CPM in the stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

C_{SO4} = Concentration of $SO_4^=$ in the sample, mg/ml.

m_b = Sum of the mass of the water and $MeCl_2$ blanks, mg.

m_c = Mass of the NH_4^- added to sample to form ammonium sulfate, mg.

m_i = Mass of inorganic CPM matter, mg.

m_o = Mass of organic CPM, mg.

m_r = Mass of dried sample from inorganic fraction, mg.

m_{rc} = Mass of dried sample from inorganic fraction corrected for volume of aliquot taken for IC analysis, mg.

V_b = Volume of aliquot taken for IC analysis, ml.

V_{ic} = Volume of impinger contents sample, ml.

7.2 Correction for NH_4^- and H_2O. Calculate the correction factor to delete the NH_4^- retained in the sample and to add the combined water removed by the acid-base reaction based on the IC $SO_4^=$.

$$m_c = K\ C_{SO4}\ V_{ic} \qquad \text{Eq. 202-1}$$

where:

K = 0.020502

7.3 Mass of Inorganic CPM.

$$m_{rc} = m_r \left[\frac{V_{ic}}{V_{ic} - V_b}\right] - m_b + m_c \qquad \text{Eq. 202-2}$$

7.4 Concentration of CPM.

$$C_{cpm} = \frac{m_o + m_i}{V_{m\ std}} \qquad \text{Eq. 202-3}$$

8. ALTERNATIVE PROCEDURES

8.1 Determination of NH_4^- Retained in Sample by Titration.

8.1.1 An alternative procedure to determine the amount of NH_4^- added to the inorganic fraction by titration may be used. After dissolving the inorganic residue in 100 ml of water, titrate the solution with 0.1 N NH_4OH to a pH of 7.0, as indicated by a pH meter. The 0.1 N NH_4OH is made as follows:

Add 7 ml of concentrated (14.8 M) NH_4OH to 1 liter of water. Standardize against standardized 0.1 N H_2SO_4 and calculate the exact normality using a procedure parallel to that described in Section 5.5 of Method 6 (Appendix A, 40 CFR Part 60). Alternatively, purchase 0.1 N NH_4OH that has been standardized against a National Institute of Standards and Technology reference material.

8.1.2 Calculate the concentration of $SO_4^=$ in the sample using the following equation.

$$C_{SO4} = \frac{48.03\ V_t\ N}{100} \qquad \text{Eq. 202-4}$$

where:

N = Normality of the NH_4OH, mg/ml.

V_t = Volume of NH_4OH titrant, ml.

48.03 = mg/meq.

100 = Volume of solution, ml.

8.1.3 Calculate the CPM as described in Section 7.

8.2 **Analysis of Chlorides by IC.** At the conclusion of the final weighing as described in Section 5.3.2.3, redissolve the inorganic fraction in 100 ml of water. Analyze an aliquot of the redissolved sample for chlorides by IC using techniques similar to those described in Method 5F for sulfates. Previous drying of the sample should have removed all HCl. Therefore, the remaining chlorides measured by IC can be assumed to be NH_4Cl, and this weight can be subtracted from the weight determined for CPM.

8.3 **Air Purge to Remove SO_2 from Impinger Contents.** As an alternative to the post-test N_2 purge described in Section 5.2.1, the tester may opt to conduct the post-test purge with air at 20 liter/min. **Note:** The use of an air purge is not as effective as a N_2 purge.

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APPENDIX B

DATA ASSESSMENT

Statistical evaluations conducted using the results from the field evaluations included: (1) determination of the precision for combined sampling and analysis; (2) comparison of the sample results for the trains subjected to a posttest purge to those having undergone no purge to evaluate the effect of the purge on the reduction of sulfates, chlorides, and organics; (3) comparison of the amount of sulfate in the final residue as determined by ion chromatography (IC) to the stoichiometric amount of sulfate in the residue as determined by ammonium hydroxide (NH_4OH) titrations; (4) comparison of the chloride content of each sample before and after it is initially taken to dryness; and (5) calculation of the collection efficiency of the impingers for condensible emissions. The methodology for performing these evaluations are explained below. Equations are also provided for calculation of the sulfate content by titration.

B.1 PRECISION OF COMBINED SAMPLING AND ANALYTICAL PROCEDURES

The precision of the combined sampling and analytical procedures was calculated from the standard deviation, and expressed as the relative standard deviation (coefficient of variance), between the results for the four trains in each quad-train run. The equations for the calculation of precision are shown below.

$$s = \left[\sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1) \right]^{1/2}$$

where

s = Standard deviation,
x_i = Result for ith sample,
$\bar{x}$ = Mean of sample results, and
n = Number of samples.

$$RSD(CV) = \frac{s}{\bar{x}}$$

where

RSD = Relative standard deviation or coefficient of variance.

In order to obtain a more accurate estimate of precision, an F test was run on the results from different quad-train runs to determine if the sample variances were homogeneous. If the variances were homogeneous, the standard deviations were pooled. Otherwise, a different precision was reported for each run.

B.2 EFFECT OF POSTTEST PURGE

The effect of the posttest purge on the results for sulfates, chlorides, and organics was determined using a matched-pair t-test. The null hypothesis, H_o, was $u_d = 0$ and H_a: $u_d = 0$, where u_d was the mean of the differences between the results for the purged trains and the unpurged trains for each quad-train run. The percent difference between the pairs of results was calculated.

B.3 COMPARISON OF SULFATES IN FINAL RESIDUE BY IC VERSUS NH_4OH TITRATION

The comparison of the results for sulfates in the final residue using IC versus NH_4OH titration for measurement was also determined using a matched-pair t-test. The null hypothesis, H_o, was $u_d = 0$ and H_a: $u_d = 0$, where u_d was the mean of the differences between the sulfates in the final residue as measured by IC and NH_4OH titration. The difference between each pair of results was also calculated as percent difference.

B.4 EFFECT OF DRYING ON CHLORIDES

The effect on the chloride content of initially taking the inorganic fraction to dryness (using heat) was determined using a matched-pair t-test. The null hypothesis, H_o, was $u_d = 0$ and H_a: $u_d = 0$, where u_d was the mean of differences between the chlorides in each sample before and after heating. The differences of the results was also calculated for each sample using the before heating result as the basis:

$$\% D = Cl^- \text{ (after)} - Cl^- \text{ (before)} / Cl^- \text{ (before)}$$

B.5 COLLECTION EFFICIENCY OF IMPINGERS FOR CONDENSIBLE EMISSIONS

The collection efficiency of the candidate train for collecting condensible emissions was calculated from the results of the third field test at a coal-fired boiler. The normal number of impingers (three) should collect greater than 99% of the emissions. Thus, an extra (collection efficiency) impinger placed after the third impinger should collect less than 1% of the sample. The equation used for calculation of collection efficiency is shown below:

$$\text{Collection efficiency} = \frac{M_{imp}}{M_{imp} + M_{eff}}$$

where

M_{imp} = Mass of sample caught in first three impingers, and
M_{eff} = Mass of sample collected in extra impinger.

B.6 SULFATE CONTENT BY TITRATION WITH AMMONIUM CHLORIDE

In some cases, the amount of sulfate in the sample as $H_2SO_4 \cdot H_2O$ was determined by titrating with 0.1 N NH_4OH to an endpoint pH 7.0. The titration produces the reaction shown below:

$$H_2SO_4 + 2\ NH_4OH \longrightarrow (NH_4)_2SO_4 + 2\ H_2O$$

The amount of sulfate in the sample was calculated using the above reaction and Technique 1 as follows:

Technique 1

H_2SO_4 = 98 mg,
2 NH_4OH = 70 mg,
$(NH_4)_2SO_4$ = 132 mg, and
2 H_2O = 36 mg.

$$\text{mg } NH_3 = \text{mL } NH_4OH \times \frac{\text{normality } NH_4OH \text{ (meq)}}{\text{mL } NH_4^+} \times \frac{35 \text{ mg } NH_4OH}{\text{meq } NH_4OH} \times \frac{17 \text{ mg } NH_3}{35 \text{ mg } NH_4OH}$$

The amount of sulfate was calculated using the above reaction and Technique 2 as follows:

Technique 2

SO_4^{-2} = 96 mg, and
$2NH_4^+$ = 36 mg.

$$\text{mg } NH_4^+ = \text{mL } NH_4OH \times \frac{\text{normality } NH_4OH \text{ (meq)}}{\text{mL } NH_4^+} \times \frac{35 \text{ mg } NH_4OH}{\text{meq } NH_4OH} \times \frac{18 \text{ mg } NH_4^+}{35 \text{ mg } NH_4OH}$$

$$\text{mg } SO_4^{-2} = \text{mg } NH_4^+ \times \frac{96 \text{ mg } SO_4^{-2}}{36 \text{ mg } NH_4^+}$$

Both calculation techniques were found to be accurate for determination of sulfate content in the sample. The weight of ammonia or ammonium added as titrant was subtracted from the gravimetric determinations to give the "corrected weights."

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16. ABSTRACT

The report describes the development and evaluation of a draft protocol for measuring condensible particulate matter (CPM) emissions. An impinger catch approach was evaluated in the laboratory and at wood-fired and coal-fired boilers. The report summarizes the approach and major findings and recommendations which resulted from the study. Test results and statistical analysis of the results are presented.

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